Supporting Information

A Facile and Scalable Route to the Preparation of Catalytic Membranes With In-situ Synthesized Supramolecular Dendrimer Particle Hosts for Pt(0) Nanoparticles Using a Low Generation PAMAM Dendrimer (G1-NH_2) as Precursor

Madhusudhana Rao Kotte[1+], Alex T. Kuvarega[1,2+], Siddulu N. Talapaneni[1], Manki Cho[1], Ali Coskun[1] and Mamadou S. Diallo[1,3*]

[1]Graduate School of Energy, Environment, Water and Sustainability (EEWS)
Korea Advanced Institute of Science and Technology (KAIST)
291 Daehak-ro, Yuseong-gu, Daejeon 34141, Republic of Korea

[2]Nanotechnolgy and Water Sustainability Research Unit
College of Science, Engineering and Technology, University of South Africa (UNISA)
UNISA Science Campus, Florida, 1709, Johannesburg, Republic of South Africa

[3]Division of Chemistry and Chemical Engineering
California Institute of Technology
1200 East California Boulevard, Pasadena, CA 91125, USA

[+]Authors with equal contributions

[±]Present address: Department of Chemistry, University of Fribourg
Av. de l'Europe, CH-1700 Fribourg, Switzerland

*Corresponding Author: Mamadou S. Diallo
E-mail: diallo@caltech.edu and mdiallokaist1@gmail.com

EXPERIMENTAL METHODS AND PROCEDURES

1) Chemicals and Materials

Polyvinylidene fluoride (PVDF) [Kynar 761] was provided by Arkema (King of Prussia, PA, USA). Samples of microporous polyethylene terephthalate (PET) membrane supports were provided by Hirose Paper (Japan). G1-NH_2 PAMAM dendrimer was purchased as methanol solution (~34 wt%) from Dendritech Inc, USA. Table S1 lists selected physical-chemical properties of the G1-NH_2 PAMAM. Analytical standard grade epichlorohydrin (ECH) [≥ 99.5% purity] was purchased from Sigma-Aldrich. Triethyl phosphate (TEP) [99% purity], ethanol (99.5% purity) and nitric acid (60 wt% HNO_3) were purchased from Daejung Chemicals (South Korea). Hydrochloric acid (12 M HCl) was purchased from Junsei (South Korea). Sodium hydroxide (NaOH pellets), and hydrogen hexachloroplatinate*(*IV*)* hexahydrate ($H_2PtCl_6.6H_2O$), analytical standard grade (≥ 99.5% purity) of cyclohexene, cyclooctene, 1-hexyne, 1-hexene, 1, 5 hexadiene, 3-hexene, chloroform-d (99.8 atom % D purity) and tetramethysilane (ACS reagent, NMR grade, ≥99.9% purity) were purchased from Sigma-Aldrich. A standard solution of platinum (Pt) [Multi-element calibration standard-3, 10 µg/mL of Sb, Au, Hf, Ir, Pd, Pt, Rh, Ru, Te, Sn in 10% HCl with 1% HNO_3] was purchased from Agilent. All chemicals were used as received. All aqueous solutions were prepared using Milli-Q deionized water (DIW) with a resistivity of 18.2MΩcm and total organic content < 5 ppb.

2) Preparation of a PVDF-PAMAM-G1 membrane with in-situ synthesized PAMAM supramolecular dendrimer particles

A PVDF-PAMAM membrane with *in situ* synthesized G1-NH_2 PAMAM supramolecular dendrimer particles (SDPs) and a control PVDF membrane (15 wt%) were prepared in this study using a combined thermally induced phase separation (TIPS) and non-solvent induced phase separation (NIPS) process. Table S2 lists the compositions of the membrane casting solutions. The membrane preparation procedures were adapted from our previous work[1] as described below.

2.1) Preparation of membrane casting solutions. A typical membrane casting solution was prepared by mixing the required amounts of PVDF and TEP (Table S2) in a three neck round-bottom flask equipped with a condenser and an overhead stirrer. A homogeneous PVDF dope solution was obtained after mixing for 24 hours at 80 °C. Following this, the as-prepared PVDF dope solution was transferred into a glass container and covered with aluminum foil.

2.2) In-situ synthesis of PAMAM supramolecular dendrimer particles (SDPs) in the PVDF dope solution. Prior to membrane casting, the PVDF dope solution was homogenized at 4000 rpm for 10 mins using a Silverson L5M high shear mixer (HSM). During the homogenization, the temperature of the dope was raised to 80 °C and kept constant. A solution of G1-NH_2 PAMAM in TEP was then added drop wise to the PVDF dope solution for 5 minutes followed by high shear mixing for 15 minutes to obtain a homogeneous PVD+PAMAM dispersion in TEP. A solution of ECH in TEP was then added drop wise to the dispersion and homogenized for 5 mins under similar HSM conditions to obtain a stable dispersion of ECH crosslinked PAMAM SDPs in the PVDF+TEP dope solution. Finally, the curing reaction was continued in a round bottom flask equipped with an overhead stirrer at 80 °C for 3 hours.

2.3) Membrane Casting. Following the completion of the curing reaction, the hot dispersion of PVDF + TEP + PAMAM SDPs (~60-80 °C) was utilized as dope to cast PVDF-PAMAM-G1 membranes. For the Pt(IV) loading studies and catalytic experiments, the membranes were cast onto PET microporous supports. In contrast, the membranes were prepared without PET supports for the characterization experiments. To prepare a membrane with a PET support, an aliquot of the hot dispersion of PVDF + TEP + PAMAM SPDs (~60-80 °C) was poured onto a PET non-woven fabric that was glued to a clean glass plate. A casting knife (BYK Chemie) [with 300 μm air gap] was used to uniformly coat the casting solution onto the PET support. The nascent PVDF-PAMAM-G1 membrane was kept for 30 seconds at ambient temperature (25 ± 1°C, RH: 55%) to initiate the first phase of the membrane formation process (TIPS) followed by immersion into a DIW bath with a temperature of 23 ± 1°C for the second phase (NIPS). After 1 hr, the nascent membrane was transferred to a fresh DIW bath and immersed for 24 h. Following this, the membrane was soaked in ethanol for 10 h. The PET supported membranes were stored in DIW with the water periodically replaced with fresh DIW until the Pt(IV) loading experiments were initiated. A similar procedure was used to prepare a PVDF-PAMAM-G1 membrane without PET support by pouring the casting solution on a clean glass plate. In this case, the unsupported membrane was peeled off from the glass plate, dried and stored in a desiccator until the characterization studies were initiated.

3) Characterization of a PVDF-PAMAM-G1 membrane with in-situ synthesized SDPS

The membrane characterization procedures were adapted from our previous work[1]. For the characterization experiments, we utilized a PVDF-PAMAM-G1 membrane with no PET support. The morphology, surface layer pore diameter, PAMAM particle size range, wettability and surface charge of the unsupported PVDF-PAMAM-G1 membrane were characterized using a broad range of assays and tools as described below.

3.1) SEM characterization. The cross section and surface layer of the PVDF-PAMAM-G1 membrane were imaged with a field emission scanning electron microscope (FESEM, Magellan Series 400, FEI Corporation) at an acceleration voltage of 2.0 kV. Before imaging, the membrane was first coated with platinum for 30 seconds followed by osmium for 30 seconds to minimize the charging effect. To obtain the cross section morphology, the membrane was frozen and fractured following immersion in liquid nitrogen. The SEM micrographs (Figures 1B and 1C; Manuscript) were subsequently analyzed to estimate membrane thickness and the size range of the membrane in-situ synthesized PAMAM particles using the Image J software[2] (Version 1.45m) [Table S3].

3.2) N_2 adsorption permporometry. The average pore diameter of the surface layer of the PVDF-PAMAM-G1 membrane was estimated by N_2 adsorption permporometry at 77 K using a Micromeritics ASAP 2020 accelerated surface area and porosimetry analyzer. The Barrett-Joyner-Halenda (BJH) methodology[3] [as implemented in the instrument software] was utilized to extract the membrane surface layer pore diameter from the N_2 adsorption/desorption data (Figure S1).

3.3) Dynamic light scattering measurements. The FESEM estimates of the size ranges of the in-situ synthesized PAMAM SDPs of the PVDF-PAMAM-G1 membrane were validated using dynamic light scattering (DLS) measurements. For this purpose, 0.2 g of dry membrane was dissolved in 20 g of TEP (a good solvent for PVDF) for 15 hours at ambient temperature. Following this, the dispersion was

sonicated for 15 minutes. A 1-mL aliquot was sampled from the dispersion and diluted with 10 mL of TEP for the DLS experiments, which were conducted at 25 °C using duplicate measurements.

3.5) Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)
The DSC and TGA studies were carried out using 5 mg samples of unsupported PVDF-PAMAM-GI and pristine PVDF membranes. The DSC measurements were conducted using a NETZSCH DSC 204 F1 instrument with a constant heating/cooling rate of 10 °C/min. Each membrane sample was first annealed by heating from 25 to 200 °C followed by cooling to 25 °C to erase its thermal history. Following this, a second cycle of heating (25 to 200 °C) was performed on each annealed sample to determine its melting temperature (T_m). This was followed by a second cooling cycle (200 to 25 °C) to determine the sample crystallization temperature (T_c). The TGA measurements were conducted in a nitrogen atmosphere (N2) using a NETZSCH TG 209 F3 instrument. For the TGA studies, each membrane sample was heated from 30 °C to 700 °C with a constant heating/cooling rate of 10 °C/min. The results of the TGA measurements were used to estimate the degradation temperatures of the PVDF-PAMAM-GI and pristine PVDF membranes.

3.6) FT-IR and x-ray photoelectron spectroscopy. The surface atomic and chemical compositions of the PVDF-PAMAM-G1 membrane were characterized by Fourier transform infrared spectroscopy (Mid and near FT-IR) and x-ray photoelectron spectroscopy (XPS). To guide the analysis of the FT-IR and XPS spectra, we prepared and tested a PVDF control membrane (Table S2). The mid IR spectra (500 cm^{-1} to 4000 cm^{-1}) of both membranes were scanned in attenuated total reflectance (ATR) mode and acquired by averaging 32 scans at a resolution of 2 cm^{-1} using a JASCO 4100 FT-IR spectrometer (Japan) and a zinc selenide ATR crystal plate with an aperture angle of 45°. In contrast, the near IR (NIR) spectra (4000 cm^{-1} to 10000 cm^{-1}) of both membranes were recorded by reflection using a Bruker MPA FT-NIR spectrometer equipped with a quartz beam splitter and an external RT-PbS detector. The NIR spectra were acquired by averaging 32 scans at a resolution of 8 cm^{-1}. The XPS studies were conducted using an SSX-100 spectrometer from Surface Science Instruments. The membrane samples were irradiated with a beam of monochromatic Al Kα X-rays with energy of 1.486 keV.

3.7) Contact angle measurements. The surface layer of the PVDF-PAMAM-G1 membrane was also characterized using a Phoenix 300 contact angle analyzer. A micro syringe was utilized to place a water droplet on the membrane surface. After 30 and 120 seconds, the image was captured and analyzed using the instrument's image processing software. The reported contact angle is the average of five different measurements.

3.8) Zeta potential measurements. The zeta potential of the PVDF-PAMAM-G1 membrane was measured using the electrophoresis method[4]. An ELSZ-2 electrophoretic light scattering spectrophotometer from Otsuka Electronics, Japan [with a plate quartz cell as membrane holder] was employed to measure the electrophoretic mobility of the monitoring particles at the surface of the PVDF-PAMAM-G1 membrane. The monitoring particles consisted of polystyrene (PS) latex particles (Otsuka Electronics, Japan) with an amide surface coating and diameter of 520 nm. The PS particles were dispersed in 0.01 M NaCl solutions at pH 7.0. The measured electrophoretic mobility (U) of the monitoring PS particles [$cm^2/(V.s)$] was utilized to calculate the membrane zeta potential (ς) [mV] using the Smoluchowski equation as given below[4]:

$$\varsigma = \frac{4\pi\eta U}{\varepsilon_r \varepsilon_0} \qquad \text{Eq. 1}$$

where η is the liquid viscosity (0.89 x 10^{-3} Pa·s), ε_r is the relative permittivity of liquid (78.38) and ε_0 is the vacuum permittivity (8.854 x 10^{-12} s·m^{-1}).

4) Pt(IV) uptake by a PVDF-PAMAM-G1 membrane with in-situ synthesized PAMAM supramolecular dendrimer particles.

The Pt(IV) extraction and loading experiments were conducted at room temperature and constant pH (7, 9 and 3) using a custom-built cross-flow ultrafiltration (UF) system (SI Figure S5). The components of the UF system were built using Teflon and polyvinyl chloride (PVC) to eliminate metal ion sorption onto the system tubing, pump head and reservoir. Based on the results of our previous investigations of Cu(II) uptake by a comparable PVDF-PAMAM-G1 membrane, we set the flow rate through the UF system at ~1.7 L/min with a cross flow velocity of ~37.2 cm/s to benchmark the kinetics of Pt(IV) extraction from solution against that of Cu(II) loading onto a similar membrane[1]. For each Pt(IV) loading experiment, we utilized a PET supported membrane coupon with a filtration area of 24 cm^2. Each Pt(IV) loading experiment consisted of four steps. First, the membrane was compacted by running deionized water (DIW) for 1 hour at a pressure of 3 bar. The pressure was then reduced to 2 bar and DIW was pumped through the membrane for 1 hour followed by membrane conditioning with the pumping of a constant pH solution of DIW + HCl or NaOH at 2 bar for 1 hour. Following this, a 2-L solution of Pt(IV) in DIW (10 mg/L) was pumped trough each membrane at 2 bar and constant pH (3, 7 and 9) for 3 hours. The initial and final volumes of the feed and permeate solutions were recorded. During each Pt(IV) loading run, aliquots (1 mL) of the feed and permeate were sampled every 5 minutes for a period of 1 hour and every 30 minutes thereafter for the remainder of the run time. The collected samples were diluted (by a factor of 100) with a 3-wt% HNO_3 solution in DIW and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) using an Agilent ICP-MS 7700x instrument. The ICP-MS instrument was calibrated using four standard solutions of Pt (10, 50, 100 and 200 ppb) that were prepared by diluting aliquots of a Pt standard solution (Multi-element calibration standard-3 from Agilent]. All standard and sample analyses were conducted in triplicates. The results of the ICP-MS analyses were utilized to determine the initial concentration of Pt(IV) in the feed (C_{Pt}^{F0}) and the concentrations of Pt(IV) in the feed and permeate at time t (C_{Pt}^{F} and C_{Pt}^{P}), respectively. The mass of Pt(IV) bound to the PVDF-PAMAM-G1 membrane (C_{Pt}^{Mem}) at time t [mg per mL of dry membrane] was expressed as:

$$C_{Pt}^{Mem} = \frac{C_{Pt}^{F0}V^{F0} - C_{Pt}^{F}V^{F} - C_{Pt}^{P}V^{P}}{A_{Mem}d_{Mem}} \qquad \text{Eq. 2}$$

where V^{F0} is the initial volume of the feed; V^{F} is the feed volume at time t; V^{P} is the permeate volume at time t; and A_{Mem} and d_{Mem} are the membrane area and thickness, respectively. For the kinetic model fit (Eq.1; Manuscript), the fraction of Pt(IV) extracted from solution by the membrane (Pt_{Mem}^{Extr}) was estimated using Eq.3 as given below:

$$Pt_{Mem}^{Extr} = \frac{C_{Pt}^{F0}}{C_{Pt}^{F}} \qquad \text{Eq. 3}$$

To gain insight into the mechanisms of Pt(IV) coordination with the ligands (e.g. secondary and tertiary amine groups) of the membrane PAMAM SDPs, a coupon of a Pt(IV) loaded PVDF-PAMAM-G1 was characterized by XPS and FT-Raman spectroscopy following completion of the metal ion loading experiments. In this case, the XPS spectrum was also acquired using an SSX-100 spectrometer (Surface Science Instruments) with the membrane sample irradiated with a beam of monochromatic Al Kα X-rays with energy of 1.486 keV. The Raman spectrum of the Pt(IV) loaded membrane coupon was collected using a FT-Raman spectrometer RFS 100/S from Bruker.

5) Preparation and characterization of a PVDF-PAMAM-G1 membrane with in-situ synthesized Pt(0) nanoparticles.

For the proof-of-concept experiments on the preparation of a membrane with in-situ synthesized Pt(0) DENs, we prepared a PET supported membrane coupon with a surface area of 24 cm^2. A two-step process was utilized to prepare the Pt(0) loaded PVDF-PAMAM-G1 membrane. First, a 2-L solution of Pt(IV) ions (10 mg/L in DIW) was pumped and recirculated thorough the membrane by cross-flow UF at pH 7 and 2 bar for 3 hours to achieve a metal ion loading of 0.525 mg per cm^2 of membrane, which yields a total Pt(IV) loading of 13 mg. Following this, the Pt(IV) loaded membrane was immersed in a sealed polypropylene (PP) centrifuge tube filled with a 50 mL solution (100 mg/L) of sodium borohydride ($NaBH_4$) in DIW under continuous mixing for 1 hour. After completion of the reactive encapsulation process, coupons of Pt(0) loaded PVDF-PAMAM-G1 membrane were characterized by XPS and FT-Raman spectroscopy as previously described in Section 4 of the SI.

The Pt(0) loaded membrane was also characterized by SEM and TEM. For the SEM imaging studies, a coupon of an unsupported PVDF-PAMAM-G1 membrane was washed with DIW (3 times) and mixed 50 mL of a 50 mg/L solution of Pt(IV) in a sealed PP centrifuge tube for an hour under continuous mixing. Following this, the Pt(IV) loaded membrane coupon was immersed in a 50 mL solution of $NaBH_4$ (100 mg/L) under continuous stirring for about an hour to reduce the Pt(IV) ions to Pt(0) nanoparticles. A FESEM (Magellan Series 400 microscope from FEI) was utilized to image the Pt(0) loaded membrane coupon at an acceleration voltage of 2.0 kV. For the TEM characterization studies, a small piece of a PET supported and Pt(0) loaded PVDF-PAMAM-G1 membrane was dissolved in 2 mL of TEP by sonication for about 30 mins. A drop of the resulting suspension was added to 2 mL of ethanol and the resulting solution sonicated for 5 mins. The sample was loaded and dried on a copper grid. Following this, the dry copper grid was mounted on a TEM (Tecnai G^2 F30 S-Twin microscope from FEI) for imaging. A high resolution TEM image (Figure 4E; Manuscript) was selected to estimate the size distribution of Pt(0) nanoparticles inside a model membrane PAMAM particle using the Image J software[2] (Version 1.45m).

6) Hydrogenation of alkenes and alkynes using a PVDF-PAMAM-G1 membrane with in-situ synthesized Pt(0) nanoparticles.

First, we investigated the hydrogenation of cyclohexene to establish the catalytic activity and recyclability of our new family of PVDF-PAMAM-G1 membranes with in-situ synthesized Pt(0) nanoparticles. For these experiments, we prepared a membrane coupon with a surface area of 24-cm^2. The membrane was cast onto a microporous PET support with a loading 0.067 mg of Pt(0) per cm^2 to achieve a total and low catalyst loading of 1.62 mg. The hydrogenation experiments were conducted in a 50 mL glass-lined stainless reactor with a magnetic stirrer and pressure control system. The reactor

was charged with 4 mL of a 2 mM solution of cyclohexane in methanol and 100 mg of the Pt/membrane that were cut into 5 small coupons. The hydrogenation of cyclohexene was carried out at room temperature and constant stirring (400 rpm) under 1 bar of H_2 for 12 hr. After the completion of the reaction, hydrogen was slowly released and the reactor was purged with N_2 gas. The reaction mixture was then filtered off and concentrated under reduced pressure using a rotary evaporator followed by ^{1}H NMR and gravimetric analyses to determine the conversion and product yield. For the ^{1}H NMR analyses, 10-mg aliquots of the substrate and final reaction mixtures were dissolved in 5 mL of d-chloroform and placed in standard NMR tubes. The ^{1}H NMR spectra were recorded on a Bruker DMX 300 MHz instrument using tetramethylsilane as reference standard.

For the regeneration and reuse studies, the Pt/membrane coupons were heated at 100 ^{o}C for 12 hr under vacuum between each reaction cycle. The Pt/membrane coupons were reused for five consecutive cycles of cyclohexene hydrogenation for a total duration of 120 hr including 60 hr of heating at 100 ^{o}C under vacuum for substrate, product and solvent removal (Figure 6; Manuscript). To gain further insight into the catalytic activity of the Pt/membrane, we evaluated the hydrogenation of five additional compounds as listed in Table 3 of the manuscript including cyclooctene, 1-hexyne, 1-hexene, 1, 5 hexadiene and 3-hexene. For these experiments, we prepared a new batch of Pt membrane coupons with PET supports and platinum loadings of 0.059 mg of Pt(0) per cm^2 to achieve a total catalyst loading of 1.43 mg. These experiments were carried out without catalyst recycling/reuse using the same procedure as implemented in the hydrogenation of cyclohexene. Thus, in each case, the reactor was charged with 4 mL of a 2 mM solution of the target compound in methanol and 100 mg of the Pt/membrane catalyst that were cut into 5 small coupons. Table 3 of the manuscript summarizes the results of the catalytic experiments.

Table S1. Selected physicochemical properties of the G1-NH_2 PAMAM dendrimer that was utilized as particle precursor for the preparation of PVDF-PAMAM-G1 membranes. The data were taken from Dendritech.[5]

Dendrimer	[a]M_{wth} (Dalton)	[b]N_{Pamine}	[c]N_{Tamine}	[d]N_{Amide}	[e]C_{Pamine} (meq/g)	[f]C_{Tamine} (meq/g)	[g]C_{Amide} (meq/g)	[h]D_H (nm)
G1-NH_2	1430	8	6	12	4.00	3.00	6.00	2.2

[a]Mwth: theoretical molecular weight.
[b]N_{Pamine}: number of primary groups.
[c]N_{Tamine}: number of tertiary amine groups.
[d]N_{Amide}: number of amide groups. Each amide group has 2 potential electron donors: 1 N donor and 1 O donor.
[e]C_{Pamine}, [f]C_{Tamine} and [g]C_{Amide} are, respectively, the concentrations of primary amine, tertiary amine and amide groups per gram of PAMAM respectively.
[h]D_H: theoretical hydrodynamic diameter of dendrimer molecule.

Table S2. Compositions of the casting dispersions and membranes that were prepared in this study.

Membrane	PVDF-PAMAM-G1		PVDF (Neat)	
	M (g)	wt (%)	M (g)	wt (%)
A. Compositions of membrane casting solutions and dispersions				
[a]PVDF	18.0	10.99	18.0	15.0
[b]PAMAM + [c]ECH	19.46	11.88	--	--
[d]TEP	120.1	73.31	102.0	85.0
[e)]PAMAM Solution (Methanol)	6.27	3.83	--	--
B. Membrane compositions (Wt% dry mass)				
PVDF	18.0	52.29	18.0	100
[1]G1-NH_2 PAMAM SDPs	16.43	47.71	--	--
C. Compositions of G1-NH_2 PAMAM supramolecular dendrimer particles (Wt% dry mass)				
ECH	7.71	39.62	--	--
PAMAM	11.75	60.38	--	--

[a]PVDF: polyvinylidene fluoride; [b]PAMAM: polyamidoamine; [c] ECH: epichlorohydrin;
[d)] TEP: triethyl phosphate; [e]Methanol solution of G1-NH_2 PAMAM (34.79 wt%).

[1]The mass fraction of G1-NH_2 PAMAM supramolecular dendrimer particles in each membrane was estimated based on the following assumptions:

i) All primary amine groups were consumed during the *in-situ* crosslinking of the supramolecular dendrimer clusters via a reaction between the epoxy and chloro groups of epichlorohydrin molecules and the primary amino groups of the G1-NH_2 PAMAM macromolecules in the dope solution (Scheme 1; Manuscript).
ii) All unreacted G1-NH_2 PAMAM macromolecules were washed away in the coagulation bath and subsequent membrane washes with methanol and DIW.

Table S3. Estimated diameters of the in-situ synthesized PAMAM particles of a PVDF-PAMAM-G1 membrane using FESEM with the image processing and analysis software ImageJ[2].

Image No	Particle Diameter (μm)
1	2.6
2	3.1
3	2.5
4	3.3
5	2.4
6	3.0
7	1.4
8	0.8
9	2.8
10	2.5
Average Diameter (μm)	2.4
Minimum (μm)	0.7
Maximum (μm)	3.3

Table S4. XPS Characterization of Pt (IV) and Pt(0) loaded PVDF-PAMAM-G1 Membranes: Summary of Results. Digital photographs and FESEM micrographs of the membranes are shown in Figures 4A-4D. The XPS spectra of the membranes are provided in Figures 5A and 5B. The binding energies and peak splits were taken from the NIST database. [6]

A. Pt 4f binding energies and peak splits

Species	BE (eV)		
	Pt $4f_{5/2}$	Pt $4f_{7/2}$	Peak Split
Pt(IV)	78.6	75.4	3.2
Pt(II)	75.8	72.9	2.9
Pt(0)	74.3	70.9	3.4

B. [a]Surface elemental composition

Element	C	N	F	O	Cl	Pt
Pt(IV) loaded membrane (Atomic %)	31.39	6.92	10.72	29.85	9.25	9.9
Pt(IV) loaded membrane (Weight %)	3.78	0.97	2.04	4.79	3.29	19.38
Pt(0) loaded membrane (Atomic %)	54.69	[b]ND	9.32	22.19	[c]ND	13.83
Pt(0) loaded membrane (Weight %)	6.29	[b]ND	1.70	3.40	[c]ND	25.85

[a]The XPS compositions are expressed in both atomic % percent and weight %.
[b]ND: Not detected.
[c]XPS atomic percentages were converted to weight percentages using an Excel-based convertor. [7]

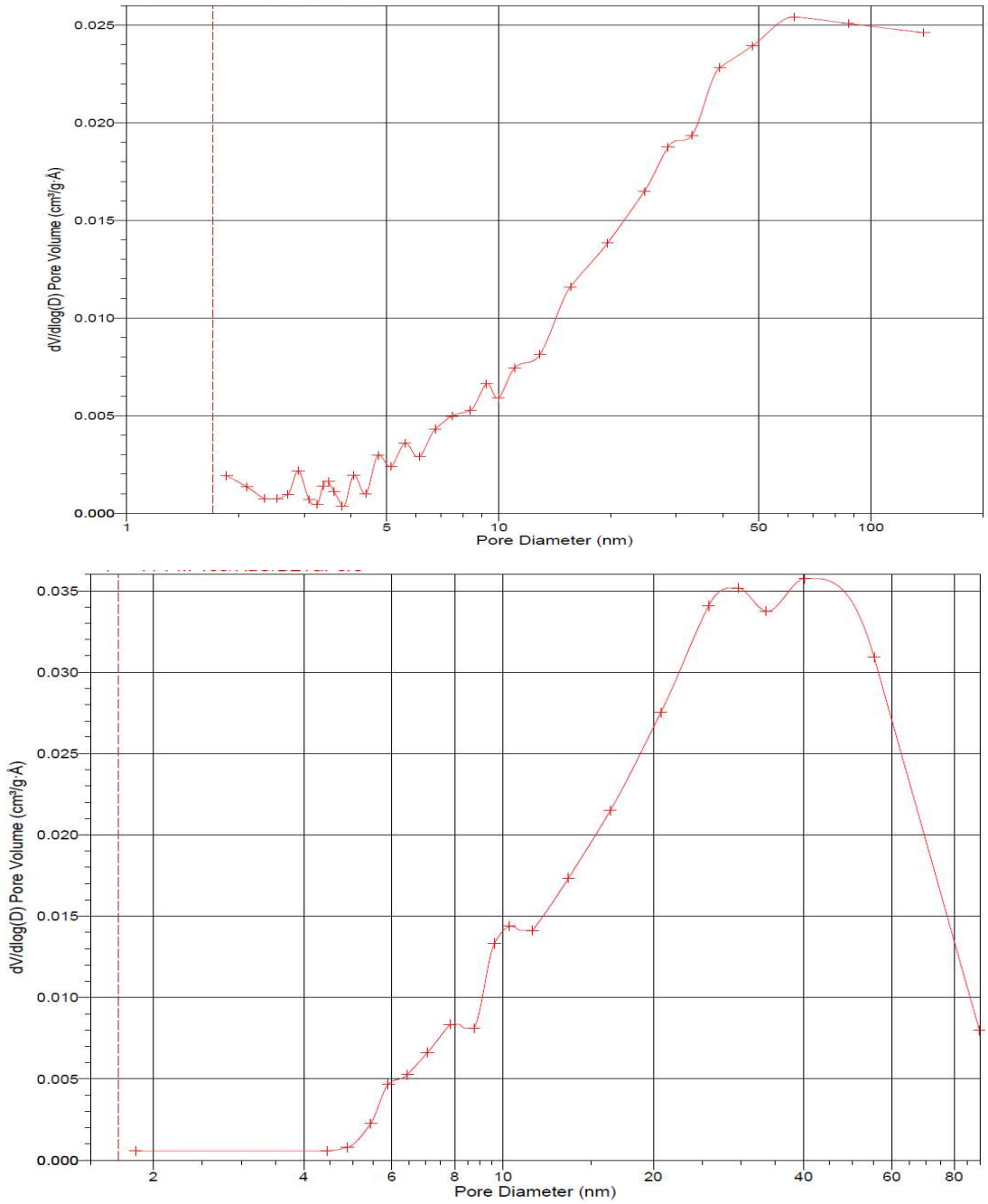
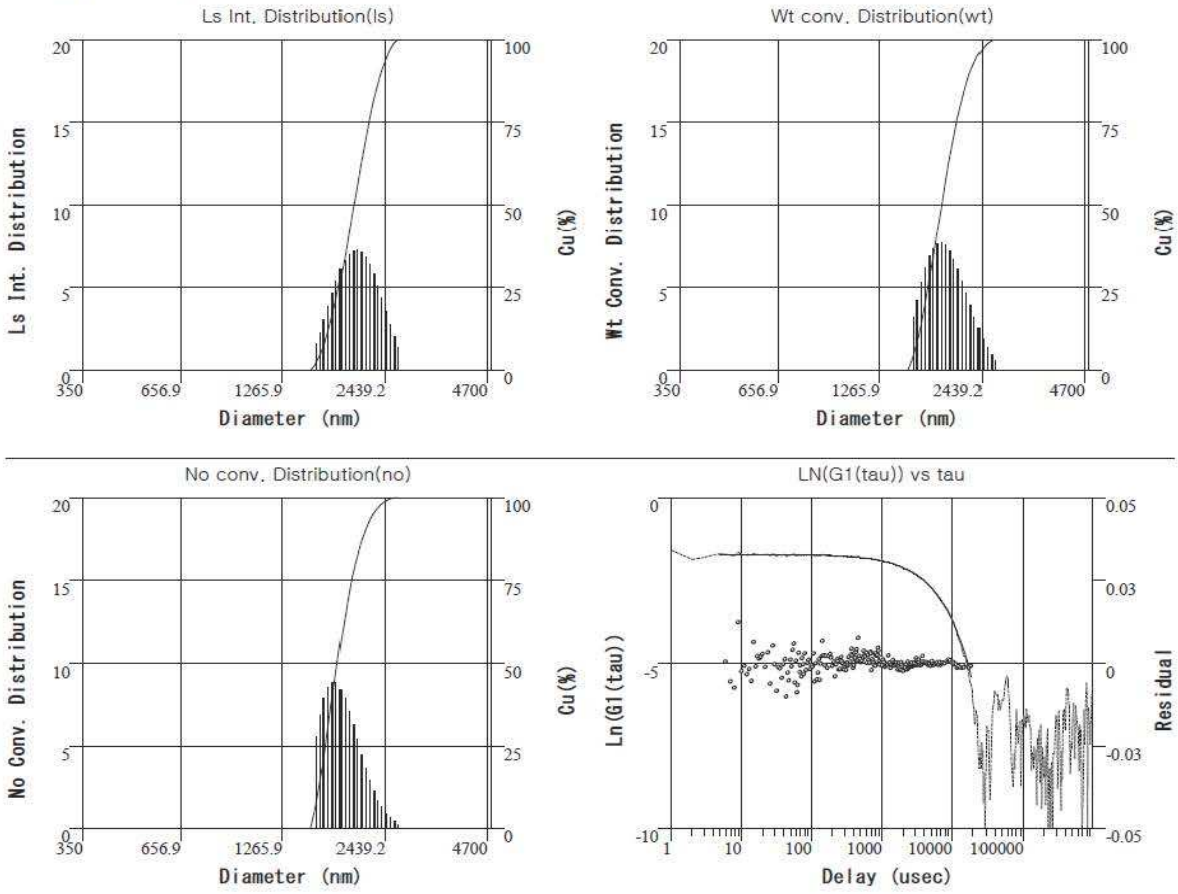


Figure S1. Characterization of a PVDF-PAMAM-G1 membrane by N_2 adsorption permporometry**.** Panel A: Barrett-Joyner-Halenda adsorption pore volume. Panel B: Barrett-Joyner-Halenda desorption pore volume. The membrane surface layer pore diameters were extracted from the N_2 adsorption data using the Barrett-Joyner-Halenda (BJH) methodology[3] as implemented in the instrument (Micromeritics ASAP 2020) data acquisition and analysis software.



//Analysis Result of Cumulant (Conventional Method)//

Diameter (d)	: 2022.5	(nm)	
Polydispersity(p.d.)	: −1.768e−00		
Diffusion Const. (D)	: 1.3949e−009	(cm2/sec)	
Residual	: 2.565e−003	(Good)	

// Measurement Condition //

Temperature	: 25.0	(deg.)
Solvent Name	: TEP	
Refractive Index	: 1.4035	
Viscosity	: 1.548	(cp)
Scattering Intensity	: 19049	(ND 7.28%)

//Histgram Result(Contin)// dw / dn = 1.04

Ls Int.(ls)			Wt conv.(wt)			No conv.(no)		
Peak	Avg.(nm)	+−Std.	Peak	Avg.(nm)	+−Std.	Peak	Avg.(nm)	+−Std.
1	2039.0	+− 258.8	1	1944.5	+− 243.5	1	1862.3	+− 218.6
2			2			2		
3			3			3		
4			4			4		
5			5			5		
Average	2039.0	+− 258.8	Average	1944.5	+− 243.5	Average	1862.3	+− 218.6

Figure S2. DLS measurements of the size range of the in-situ synthesized PAMAM particles of a PVDF-PAMAM-G1 membrane. For the DLS experiments, the membrane was dissolved in TEP.

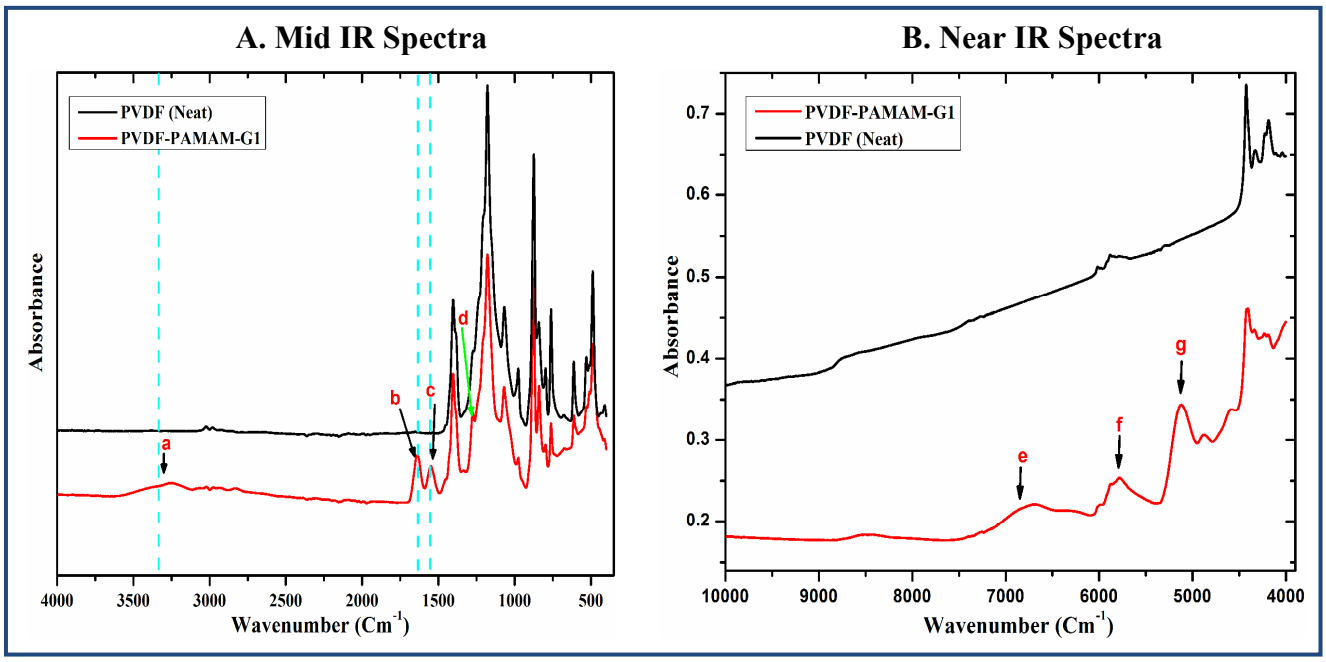
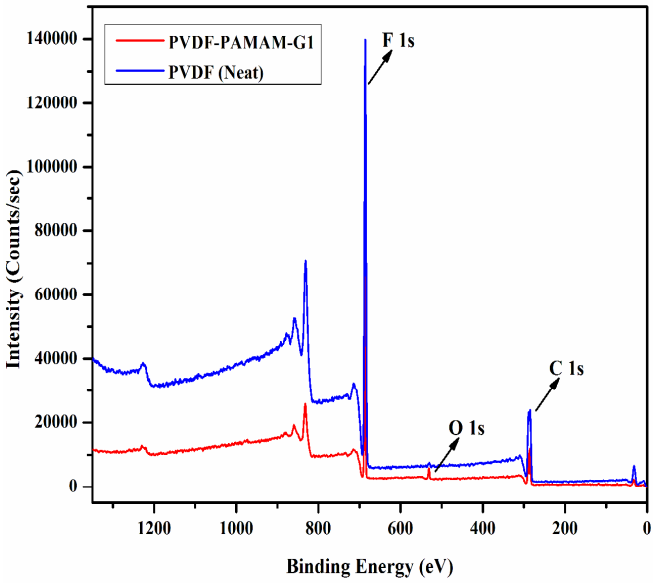


Figure S3. FT-IR spectra of PVDF-PAMAM-G1 and pristine PVDF membranes. For the FT-IR experiments, the membranes were prepared without PET supports. The FT-IR spectrum of the PVDF-PAMAM-G1 membrane exhibits several new absorption bands that are consistent with the presence of ECH cross linked PAMAM dendrimer particles at the membrane surface. Panel A highlights the main absorption bands of the mid IR region: (a) 3313 cm^{-1}: -OH and –NH stretch from amide, secondary amino or hydroxyl groups of PAMAM particles; (b) 1640 cm^{-1}: -C=O stretch from amide groups of PAMAM particles; (c) 1540 cm^{-1}: -NH bending from the amide/amine groups of PAMAM particles and (d) 1270 cm^{-1}: -C-N stretch from the amine groups of PAMAM particles. Panel B highlights the main absorption bands of the near IR region: (e) 6850 cm^{-1}: -OH overtone from the ECH crosslinked PAMAM particles. (f) 5788 cm^{-1}: overtones of –CH/-CH_2 stretching from the ECH crosslinked PAMAM particles and (g) 5116 cm^{-1}: combination of asymmetric OH stretching/bending from the ECH crosslinked PAMAM particles. The estimated composition of each membrane is listed in Table 1.

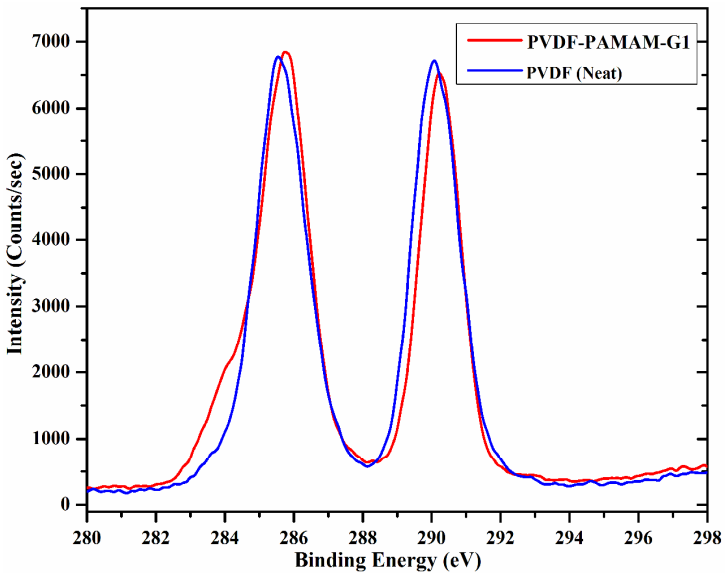
A.



B.

Membrane	XPS Atomic concentration (%)			
	C	F	O	N
PVDF-PAMAM-G1	52.62	43.1	3.81	0.47
PVDF (Neat)	51.71	48.29	-	-

C.



D.

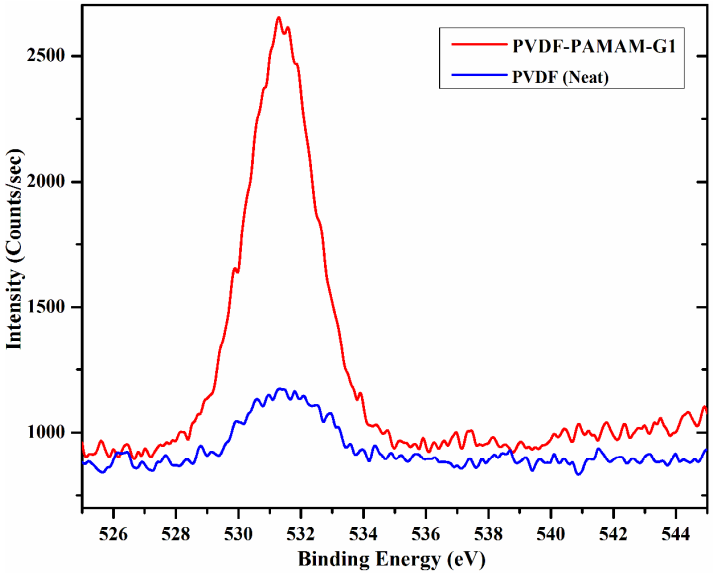


Figure S4. XPS spectra of a PVDF-PAMAM-G1 and control PVDF membranes**.** 1) Panel A: Overall scan; 2) Panel B: Surface composition; 3) Panel C: C1s scans and 4) Panel D: O1s scans

Figure S5. Digital picture of the cross-flow ultrafiltration (UF) system used in the Pt(IV) loading and extraction experiments. The filtration cell (l7.62 cm in length; 2.54 cm in width and 0.3 cm in depth), pump head, reservoir and tubing were built using Teflon and polyvinyl chloride to eliminate metal ion sorption onto the system components.

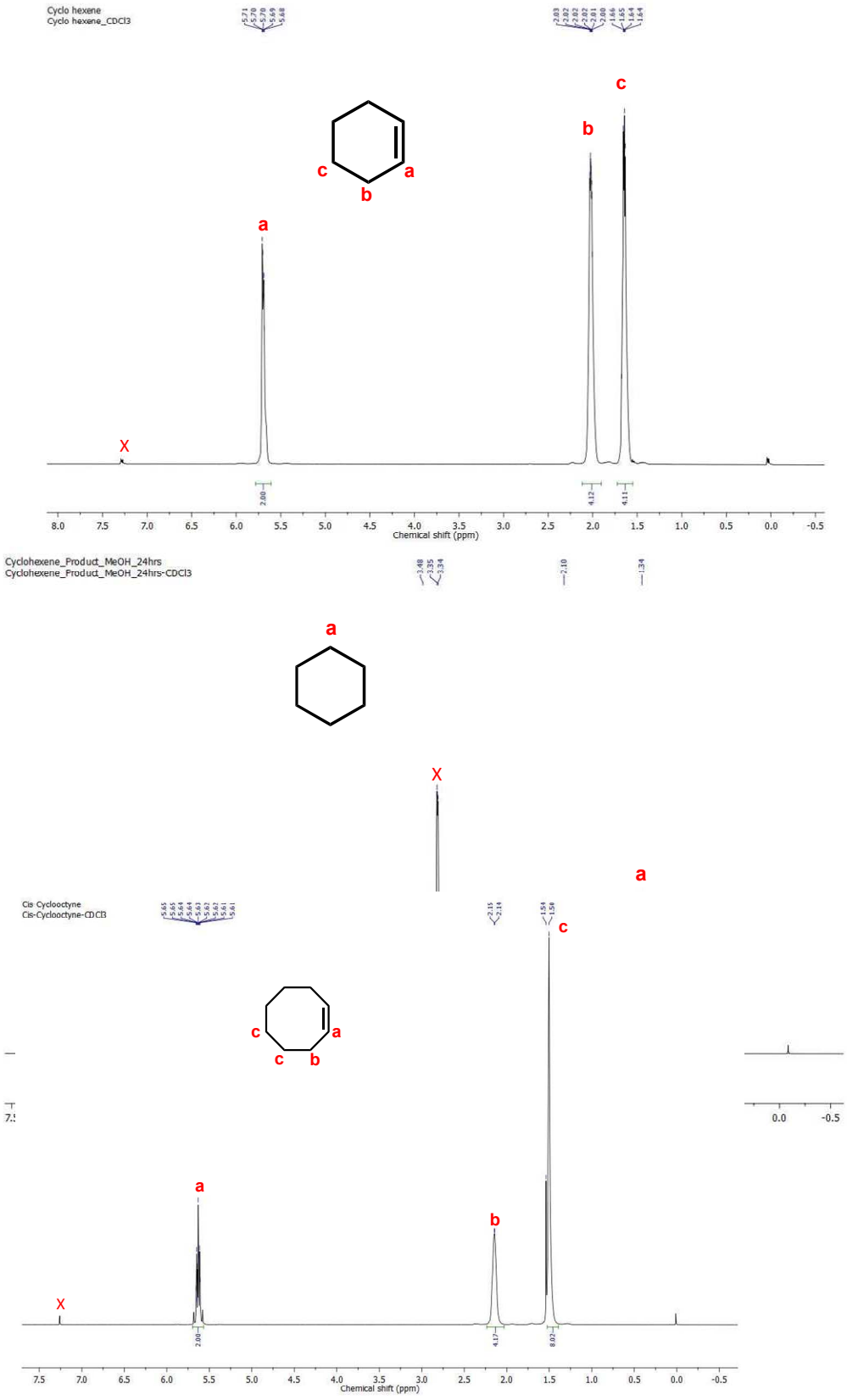


Figure S6. Hydrogenation of cyclohexene using PVDF-PAMAM-G1 membrane coupons with in-situ synthesized Pt(0) nanoparticles. Supporting ^{1}H NMR spectra and assignments: Cyclo hexene ^{1}H NMR (300 MHz, $CDCl_3$) = a δ 5.71 (*m*, 2H), b δ 2.03 (*m*, 4H), c δ 1.66 (*m*, 4H) ppm; Cyclo hexane ^{1}H NMR (300 MHz, $CDCl_3$) = a δ 1.34 (*s*, 1H) ppm.

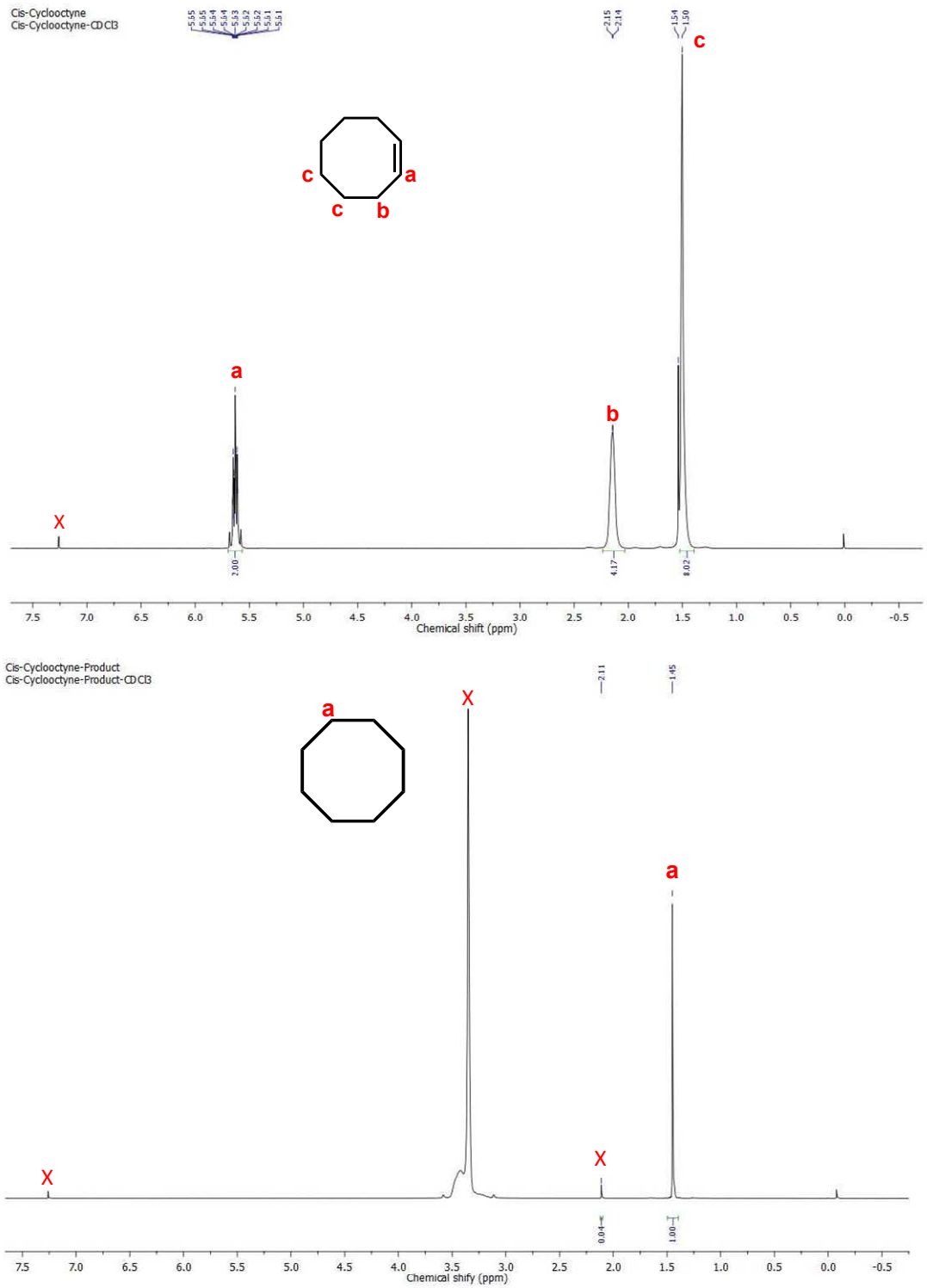


Figure S7. Hydrogenation of cis-cyclooctene using PVDF-PAMAM-G1 membrane coupons with in-situ synthesized Pt(0) nanoparticles: Supporting ^{1}H NMR spectra: Cyclo octene ^{1}H NMR (300 MHz, $CDCl_3$) = a δ 5.65 (*m*, 2H), b δ 2.15 (*m*, 4H), c δ 1.54 (*m*, 8H) ppm; Cyclo octane ^{1}H NMR (300 MHz, $CDCl_3$) = a δ 1.45 (*s*, 1H) ppm.

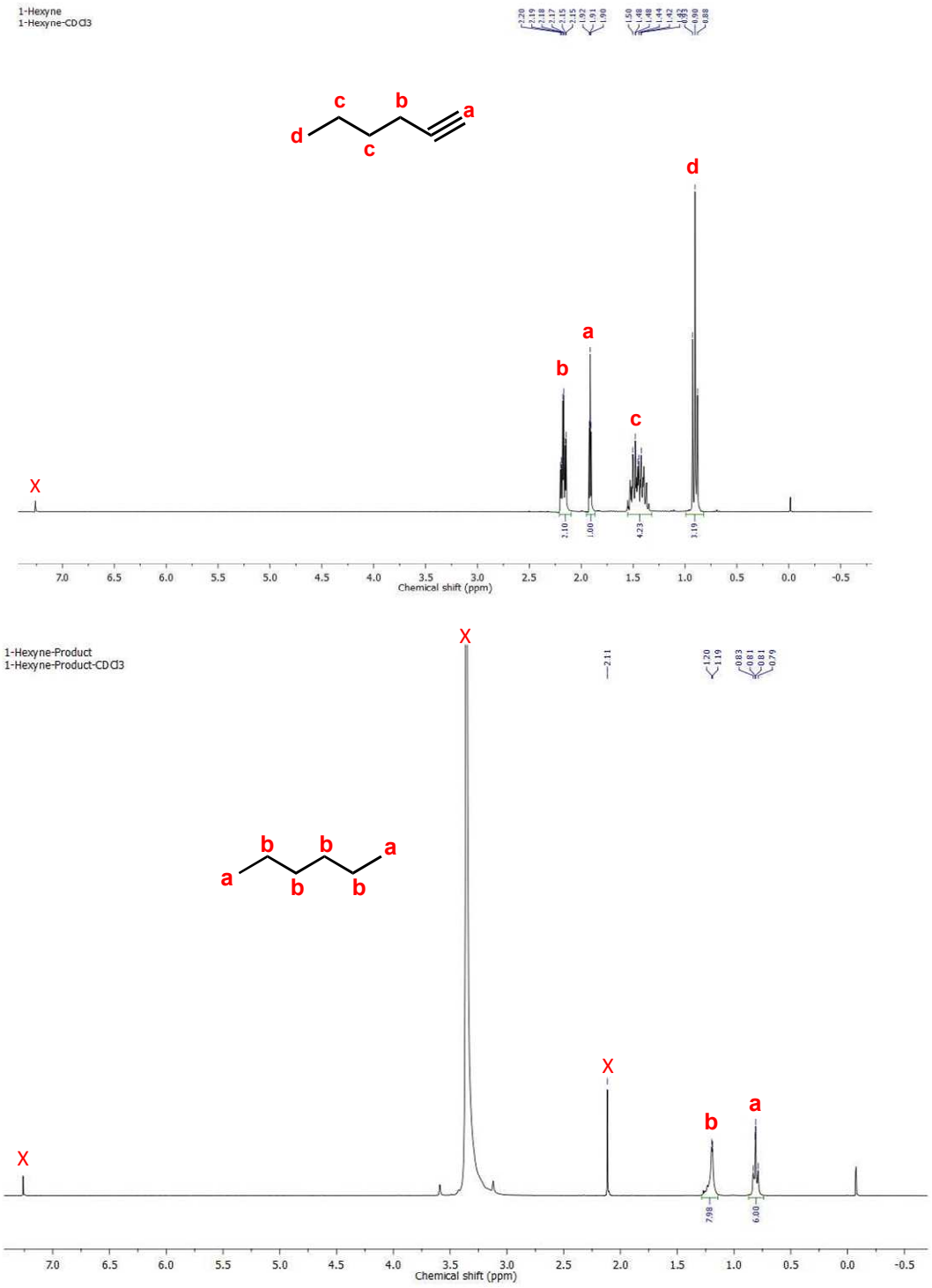


Figure S8. Hydrogenation of 1-hexyne using PVDF-PAMAM-G1 membrane coupons with in-situ synthesized Pt(0) nanoparticles: Supporting ^{1}H NMR spectra: 1-Hexyne ^{1}H NMR (300 MHz, $CDCl_3$) = a δ 1.92 (*d*, *J*=6 Hz, 1H), b δ 2.2 (*m*, 2H), c δ 1.50 (*m*, 4H), d δ 0.93 (*t*, *J*=15 Hz, 3H) ppm; *n*-Hexane ^{1}H NMR (300 MHz, $CDCl_3$) = b δ 1.20 (*br*, 8H), a δ 0.83 (*t*, *J*=12 Hz, 6H) ppm.

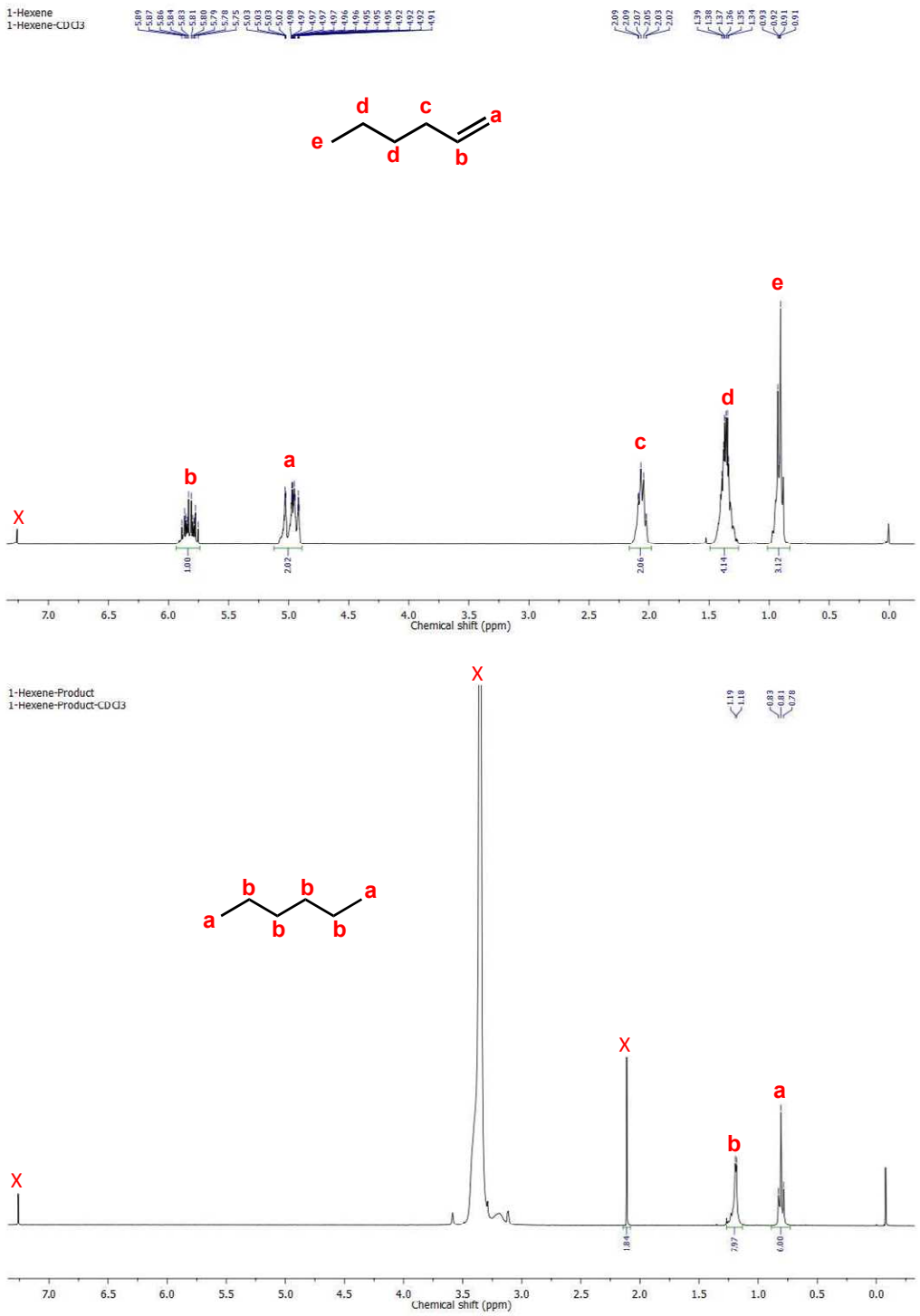


Figure S9. Hydrogenation of 1-hexene using PVDF-PAMAM-G1 membrane coupons with in-situ synthesized Pt(0) nanoparticles: Supporting ^{1}H NMR spectra: 1-Hexene ^{1}H NMR (300 MHz, $CDCl_3$) = a δ 5.03 (*m*, 2H), b δ 5.89 (*m*, 1H), c δ 2.09 (*m*, 2H), d δ 1.39 (*m*, 4H), e δ 0.93 (*t*, *J*=6 Hz, 3H) ppm; *n*-Hexane ^{1}H NMR (300 MHz, $CDCl_3$) = b δ 1.19 (*br*, 8H), a δ 0.83 (*t*, *J*=12 Hz, 6H) ppm.

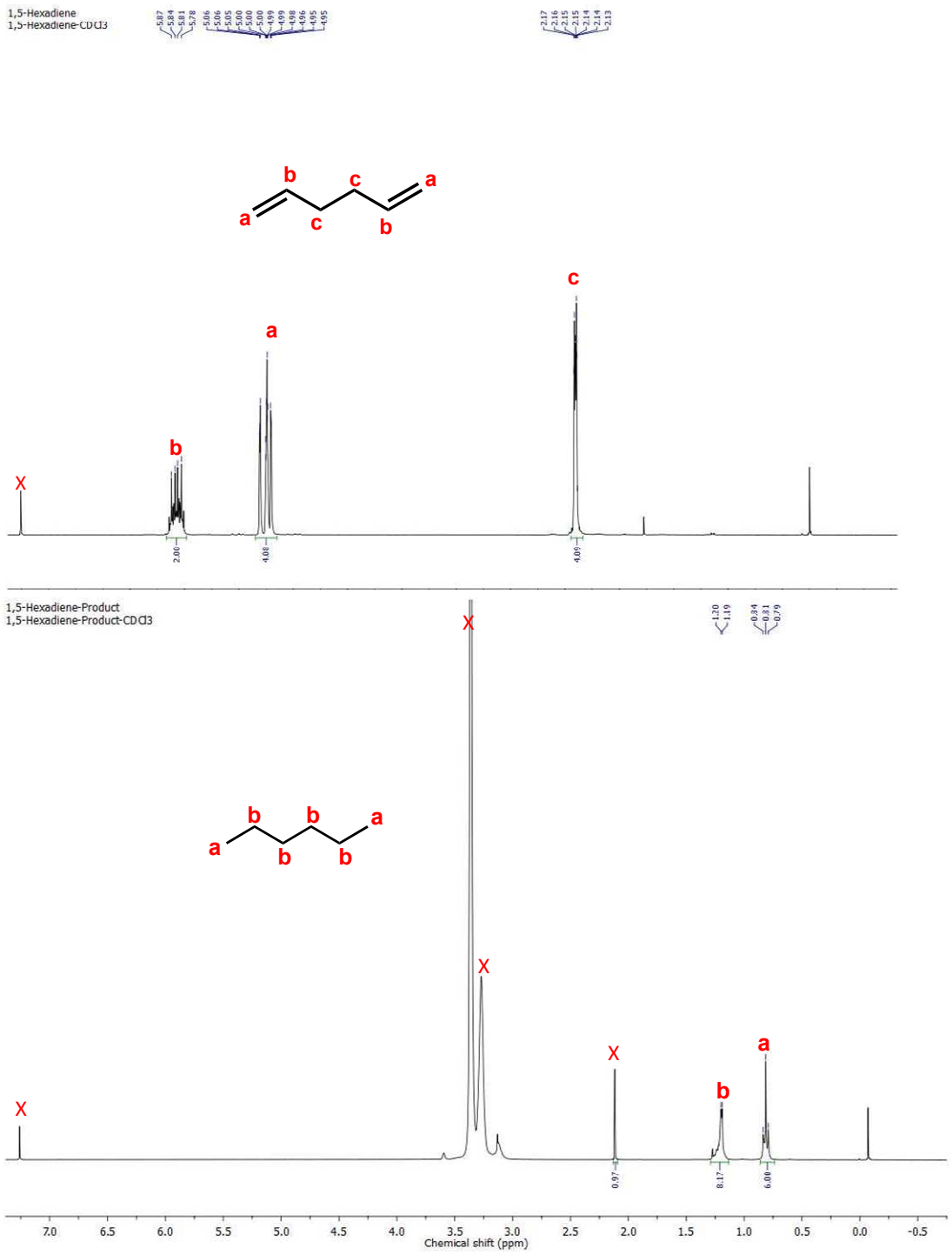


Figure S10. Hydrogenation of 1, 5-hexadiene using PVDF-PAMAM-G1 membrane coupons with in-situ synthesized Pt(0) nanoparticles: Supporting ^{1}H NMR spectra: 1,5-Hexadiene ^{1}H NMR (300 MHz, $CDCl_3$) = a δ 5.06 (*m*, 4H), b δ 5.87 (*m*, 2H), c δ 2.17 (*m*, 4H) ppm; *n*-Hexane ^{1}H NMR (300 MHz, $CDCl_3$) = b δ 1.20 (*br*, 8H), b δ 0.84 (*t*, *J*=12 Hz, 6H) ppm.

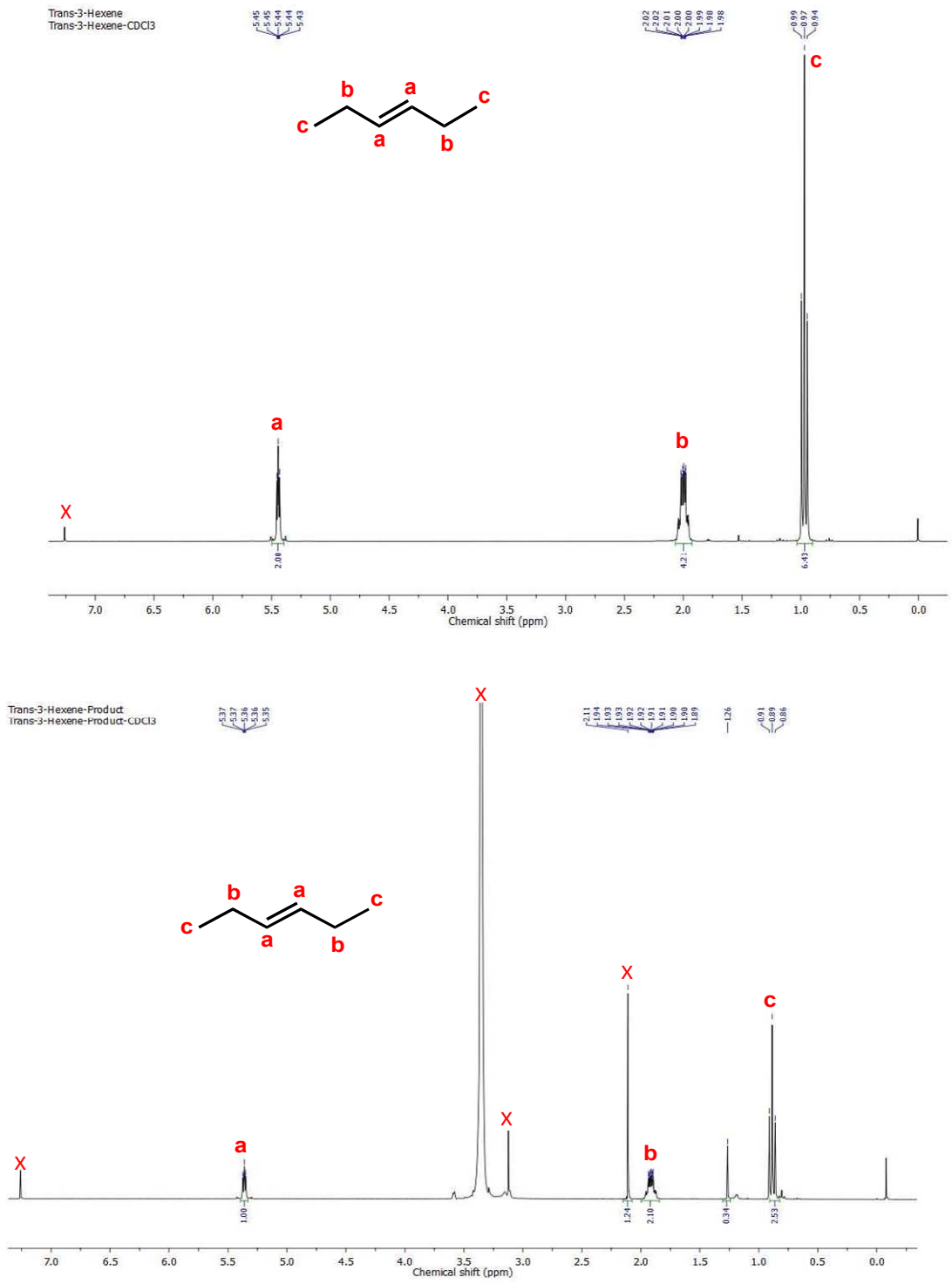


Figure S11. Hydrogenation of 3-hexene using PVDF-PAMAM-G1 membrane coupons with in-situ synthesized Pt(0) nanoparticles: Supporting ^{1}H NMR spectrum: 3-Hexene ^{1}H NMR (300 MHz, $CDCl_3$) = a δ 5.37 (*m*, 1H), b δ 2.02 (*m*, 2H), c δ 2.17 (*t*, *J*=15 Hz, 2H) ppm.

REFERENCES

1. Kotte, M. R.; Kuvarega, A.; Cho, M.; Mamba, B. B and Diallo, M. S. Mixed matrix PVDF Membranes with In Situ Synthesized PAMAM Dendrimer-like Particles: A New Class of Sorbents for Cu(II) Recovery from Aqueous Solutions by Ultrafiltration. *Environ. Sci. Technol.* **2015**, 49, 9431-9442.
2. Abramoff, M.D.; Magalhaes, P.J. and Ram, S.J. Image Processing with Image J Software. *Biophotonics. Int.* **2004**. 11, 36–42.
3. E.P. Barrett, L.G. Joyner, P.P. Halenda, The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms, *J. Am. Chem. Soc*. **1951**, 73, 373–380.
4. Park, S., Cheedrala, R. K., Diallo, M. S., Kim, Ch., Kim, I. S. and Goddard, W. A. III. Nanofiltration Membranes Based on Polyvinyldene Fluoride Nanofibrous Scaffolds and Crosslinked Polyethyleimine Networks. *J. Nanopar Res.* **2012.** 14, 884.
5. Dendritech. Technical Grade PAMAM Dendrimers. Available online at http://www.dendritech.com/pricing.html. Accessed on June 25, 2018.
6. NIST X-ray Photoelectron Spectroscopy Database. NIST Standard Reference Database 20, Version 4.1. Available online at https://srdata.nist.gov/xps/Default.aspx. Accessed on June 26, 2018.